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Room temperature chemical bath deposition of Sb_2Se_3 thin films from alkaline medium

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Abstract Room temperature (300 K) deposition of antimony triselenide thin films has been carried out onto glass substrates using simple and less expensive chemical bath deposition (CBD) method. These films are characterized by means of structural, optical and electrical properties. X-ray diffractogram shows that Sb_2Se_3 films consist of fine grains or nanoparticles. These films are smooth and homogeneous from optical microphotographs and nanocrystalline as seen from SEM images. The bandgap estimated from optical absorption is found to be 1.8 eV. The room temperature dark electrical resistivity is of the order of 10^6 Ω-cm with n-type electrical conductivity.

Keywords Semiconductor, antimony triselenide thin film, chemical bath deposition

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1. Introduction

Antimony triselenide is a layer structured semiconductor with orthorhombic crystal structure. Sb_2Se_3 thin films have attracted wide attention, due to their good photovoltaic properties and high thermoelectric power (TEP), which allow possible applications for optical and thermoelectric cooling devices. Shimakawa [1] and Tichy *et. al.* [2] have proposed an empirical relation to interpret the compositional dependence of the optical gap in the amorphous semiconducting alloys of SbSe. A few studies on the transport and optical properties of Sb_xSe_{1-x} [2, 3] and SbSe [4-7] have been carried out. Voutsas *et. al.* [8] have determined the crystal structure of Sb_2Se_3 to be orthorhombic. An experimental investigation of the electrical conductivity, thermoelectric power and magnetic susceptibility of solid and liquid Sb_2Se_3 over a wide temperature range was conducted by Glazov and Faradzhov [9]. Wood *et. al.* [10] and Shaffer *et. al.* [11] carried out comparative study of properties of crystalline and amorphous Sb_2Se_3. Torane *et. al.* [12] and Desai and Ganage [13] have deposited polycrystalline Sb_2Se_3 thin films onto FTO coated glass substrates by means of electrodeposition method. Pramanik and Bhattacharya [14] have reported a chemical bath method for the deposition of Sb_2Se_3 thin films and the specific resistance of amorphous Sb_2Se_3 is of the order of 10^7 Ω-cm with an optical bandgap of 1.88 eV.

In the present investigation, Sb_2Se_3 thin films have been deposited by using simple and less expensive chemical bath deposition (CBD) method. The preparative parameters such as concentration, volume, complexing agent and deposition time are optimized to get nanocrystalline Sb_2Se_3 thin films. The films are characterized by means of structural, optical and electrical properties.

2. Experimental

Thin films of antimony triselenide were prepared onto glass substrates from an alkaline bath (pH = 10.5) using sodium selenosulphite (Na_2SeSO_3) as selenide ion source and triethanolamine (TEA) as a complexing agent at room temperature (300 K).

A 10 ml of (0.2 mol. lit.$^{-1}$) of Sb^{3+} (antimony potassium tartarate) solution was taken in a beaker of 25 ml capacity. To this, 1 ml of triethanolamine (TEA) was added with 0.1 ml of hydrazine hydrate (80%) and then, with constant stirring, 6 ml (0.1 mol. lit^{-1}) Se^{2-} (sodium selenosulphite) solution was added. The beaker was kept at room temperature (300 K). The cleaned glass substrate was kept immersed in the reaction mixture. After

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about 4 hours, the colour of the reaction mixture turned out as reddish brown. The beaker was kept for about 10 hours. After 10 hours, the film was taken out, washed with double distilled water, dried and left in a dark desiccator.

The film thickness was measured by gravimetric weight difference method assuming bulk density of Sb_2Se_3 as 5.81 g/cm^3. The thickness (t) is given by

$$t = (m / \rho A), \quad (1)$$

where m is the mass of the film, A is the surface area and ρ is the density of the material.

The Sb_2Se_3 film was characterized by means of X-ray diffractometer PW – 3710, in the scanning angles 10 – 100° with CuKα radiation (λ = 1.5406 Å). The surface morphological study was carried out with the optical microscope Leitz Orthoplan (Germany) and scanning electron microscope, LEICA S 440i. The optical absorption measurement was carried out within 350-850 nm wavelength range by Hitachi – 330 (Japan) UV-VIS-NIR, spectrophotometer. The electrical resistivity was measured in the temperature range 335-428 K by employing a d.c. two point probe method. Silver paste was employed to ensure good ohmic contact. The working temperature was sensed by means of calibrated Cr-Al thermocouple.

3. Results and discussion

3.1 Reaction mechanism :

The formation of Sb_2Se_3 involves following steps. In the reaction mixture, the hydrolysis of sodium selenosulphite takes place which releases selenide ions as

$$Na_2SeSO_3 + OH^- \rightleftharpoons Na_2SO_4 + HSe^-, \quad (2)$$

$$HSe^- + OH^- \rightleftharpoons H_2O + Se^{2-}. \quad (3)$$

These release of Sb^{3+} ions from complexed potassium antimony tartarate as

$$[Sb^{3+}(TEA)] \rightarrow Sb^{3+} + (TEA). \quad (4)$$

Sb^{3+} ions reacted with Se^{2-} ions as

$$2\,Sb^{3+} + 3Se^{2-} \rightarrow Sb_2Se_3. \quad (5)$$

Thus, Sb_2Se_3 film formation takes place on the substrate surface due to adsorption of Sb^{3+} ions and reaction with Se^{2-} ions.

3.2 Optimization of the preparative parameters :

For the optimization of concentration of potassium antimony tartarate, concentration of potassium antimony tartarate was varied by keeping concentration of sodium selenosulphite as 0.1 M (10 ml) with (1 ml) triethanolamine (TEA) and deposition time as 10 hours. The pH was maintained ~ 10.5 by adding (0.1 ml) hydrazine hydrate and corresponding Sb_2Se_3 film thickness was measured. Figure 1 shows variation of Sb_2Se_3 film thickness with different concentrations of potassium antimony tartarate. It is found that film formation starts after 0.1 M concentration of potassium antimony tartarate or Sb^{3+} ions when ionic product exceeds the solubility product and thickness reaches a maximum value at 0.2 M. After 0.2 M concentration, average Sb_2Se_3 film thickness goes on decreasing due to the less rate of the film formation than the rate of bulk precipitation. Therefore, concentration of potassium antimony tartarate was fixed as 0.2 M.

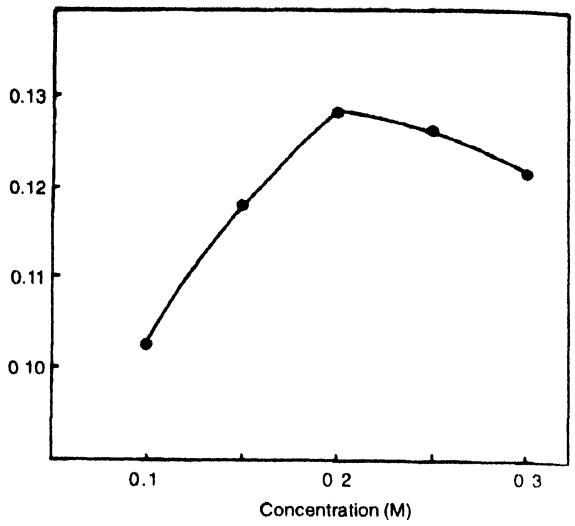


Figure 1. Variation of Sb_2Se_3 film thickness with concentration of potassium antimony tartarate with (0.1 M) sodium selenosulphite (10 ml), hydrazine hydrate (0.1 ml), TEA (1 ml) and deposition time 10 hours.

Variation of Sb_2Se_3 film thickness with various volumes of (0.1 M) sodium selenosulphite and by keeping all other parameters fixed, such as (0.2 M) potassium antimony tartarate (10 ml), hydrazine hydrate (0.1 ml), TEA (1 ml) and deposition time 10 hour is shown in Figure 2. It is found that the Sb_2Se_3 film

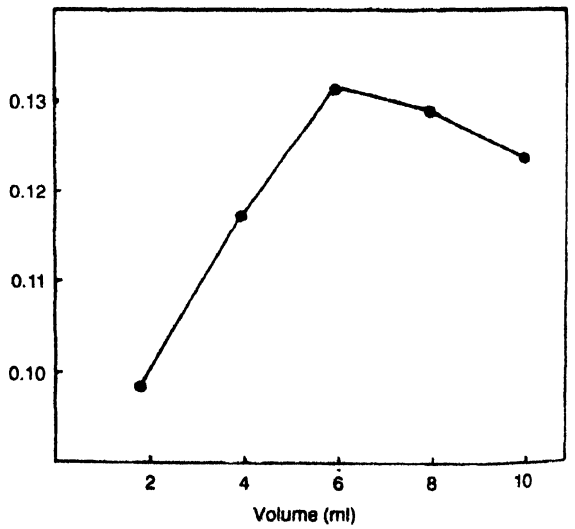


Figure 2. Variation of Sb_2Se_3 film thickness with volume of (0.1 M) sodium selenosulphite with (0.2 M) potassium antimony tartarate (10 ml), hydrazine hydrate (0.1 ml), TEA (1 ml) and deposition time 10 hours.

thickness attains maximum value at (6 ml) volume of sodium selenosulphite.

Figure 3 shows variation of film thickness with deposition time. Maximum film thickness is obtained at deposition time of 10 hours by keeping all other parameters constant as (0.2 M) potassium antimony tartarate (10 ml), (0.1 M) sodium selenosulphite (6 ml), hydrazine hydrate (0.1 ml) and TEA (1 ml).

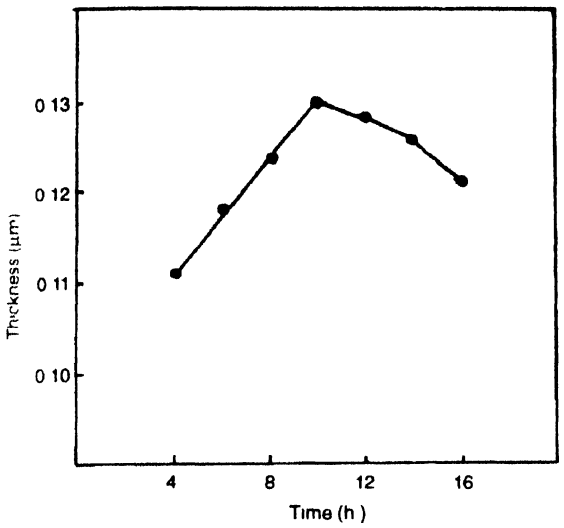


Figure 3. Variation of Sb_2Se_3 film thickness with deposition time, with (0.2 M) potassium antimony tartarate (10 ml), (0.1 M) sodium selenosulphite (6 ml), hydrazine hydrate (0.1 ml), TEA (1 ml).

3.3 Characterization of Sb_2Se_3 thin films :

Structural studies :

Figure 4 shows XRD pattern of as-deposited Sb_2Se_3 thin film onto glass substrate. XRD study reveals that film formed is of Sb_2Se_3 with orthorhombic crystal structure, with only one reflection (021) of Sb_2Se_3. The low intensity reflection indicates fine grain or nanoparticle nature of Sb_2Se_3 material.

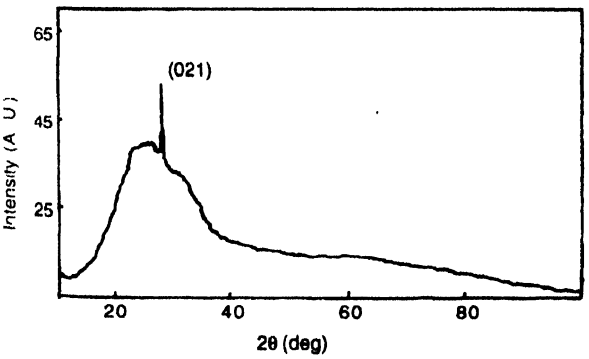


Figure 4. XRD pattern of as-deposited Sb_2Se_3 thin film onto glass substrate.

Surface morphology :

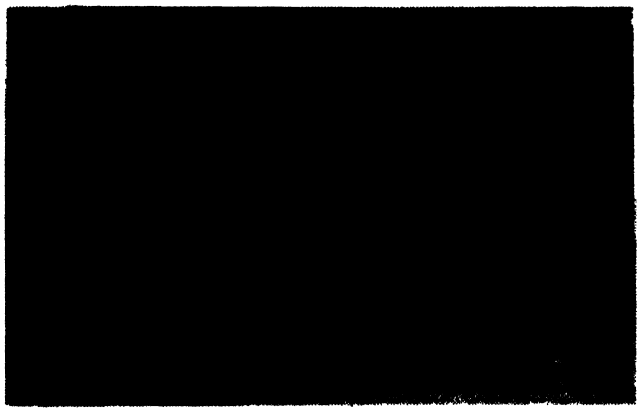
Optical micrograph of Sb_2Se_3 thin film at magnification 160 X is as shown in Figure 5(a). The Sb_2Se_3 film is relatively smooth and homogenous. Figure 5(b) shows scanning electron micrograph of Sb_2Se_3 thin film at the magnification 20,000X. The film is well covered over the substrate surface. The grain size of Sb_2Se_3 thin film is estimated by Cottrell's method [15]. This method relates the number of intercepts of grain boundaries per unit length P_L and is given by

$$P_L = (n / 2\pi r) M \tag{6}$$

where n is the total number of intercepts and M is the magnification and r is the radius of circle. Using P_L the grain size L, was determined, since

$$L = [1 / (P_L - 1)]. \tag{7}$$

The estimated average grain size of Sb_2Se_3 by using above method was between 45-50 nm which is in good agreement with the grain size (27 nm) estimated by Scherrer's formula from XRD studies.



(a)

(b)

Figure 5. (a) Optical micrograph of Sb_2Se_3 thin film at magnification 160 X and (b) Scanning electron micrograph of Sb_2Se_3 thin film at magnification 20,000 X.

3.4 Optical absorption studies :

The variation of optical absorbance (αt) with wavelength (λ) is shown in Figure 6.

The absorption data were analyzed using the following classical relation for near-optical absorption in semiconductors

$$\alpha = \frac{K(h\nu - Eg)^{n/2}}{h\nu} \quad (8)$$

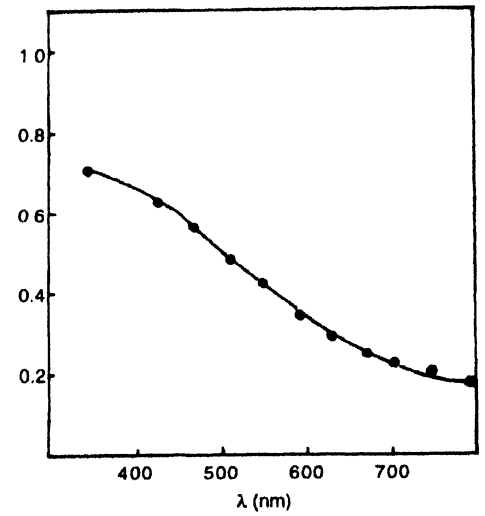


Figure 6. Plot of optical absorbance (αt) *versus* wavelength (λ) for Sb_2Se_3 thin film onto glass substrate.

where K is constant, Eg is the separation between the valence band and conduction band, n is a constant equal to 1 for direct gap semiconductor and 4 for indirect gap materials. The variation of $(\alpha h\nu)^2$ *versus* $h\nu$ [Figure 7] is linear, which means that the mode of transition in these films is of direct nature. Extrapolation of the straight line part on the energy axis for zero absorption gives the optical energy gap (Eg) as 1.80 eV for Sb_2Se_3 thin film, which is in good agreement with the earlier report as (1.88 eV) by Pramanik and Bhattacharya [14].

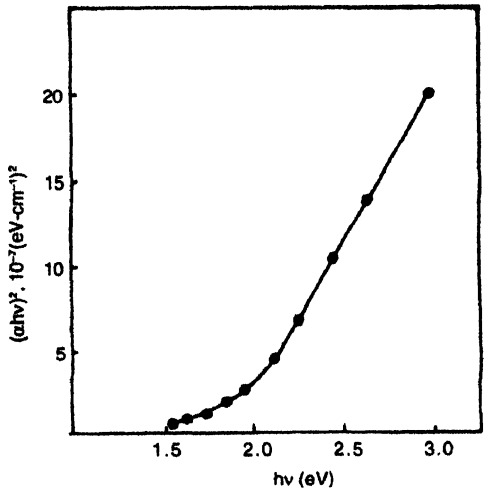


Figure 7. Variation of $(\alpha h\nu)^2$ against $h\nu$ for Sb_2Se_3 thin film (derived from Figure 6).

3.5 *Electrical resistivity measurement*

The electrical resistivity measurement by two point probe method was carried out within temperature range 335 – 428 K. The dark electrical resistivity of Sb_2Se_3 film was of the order of 10^6 Ω-cm at room temperature (27°C), which is less by one order than earlier reported value [14]. This may be due to the difference between amorphous (as reported by Pramanik and Bhattacharya) and nanocrystalline nature of the Sb_2Se_3 films. The higher value of resistivity may be attributed to nanocrystallinity of film or grain boundary discontinuities, presence of surface states and the small thickness of the film. The variation of log ρ with 1/T [Figure 8] indicates the semiconducting nature of the film. Activation energy for the electrical conduction determined from the plot is found to be 0.74 eV and is in good agreement with the earlier reported value (0.77 eV) of spray pyrolyzed Sb_2Se_3 thin films [7].

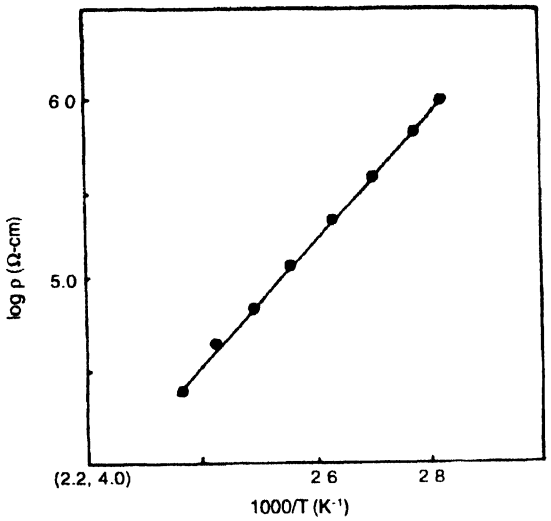


Figure 8. Variation of log ρ against 1/T for Sb_2Se_3 thin film

3.6 *Thermo* emf *measurement:*

From the thermo emf measurement, it is found that the polarity of the thermally generated voltage at the hot end is positive indicating Sb_2Se_3 films are of n-type, similar to those observed

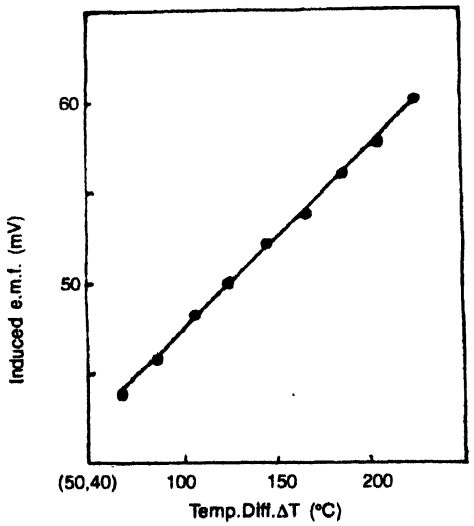


Figure 9. Plot of induced emf *versus* temperature difference (Δ T) for Sb_2Se_3 thin film.

by Bhattacharya and Pramanik [16]. The dependence of thermo emf (induced emf) on temperature difference is depicted in Figure 9. The plot shows that the increase in temperature difference results in increase in induced emf. This is attributed to the increase in carrier concentration and / or mobility of charge carriers with rise in temperature. The observed value of thermoelectric power (TEP) is 0.11 mV / K.

4. Conclusions

Sb_2Se_3 thin films are deposited by simple and less expensive chemical bath deposition method. XRD study reveals that Sb_2Se_3 films consist of fine grains or nanoparticles which is also supported by SEM images. The optical bandgap is found to be ..8 eV. The room temperature dark electrical resistivity is of the order of 10^6 Ω-cm with n-type electrical conductivity.

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